

# PATENT SPECIFICATION

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## NO DRAWINGS

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## (54) A PROCESS FOR REDUCING HAZE IN BEER

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Cheshire, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed,

reduction, particularly when under some circumstances this can be accompanied by increased efficiency, and without a reduction in desirable characteristics such as flavour and head-retention is attractive. In addition, some food purity laws require that no soluble

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## ERRATA

### SPECIFICATION No. 1,215,928

- |    |     |  |   |
|----|-----|--|---|
| 10 | i   |  | <b>ERRATA</b>                                   |
|    | p.  |  |   |
|    | t   |  |   |
|    | l.  |  | Page 1, line 86, for "redposition" read "re-    |
| 15 | t   |  | deposition"                                     |
|    | c   |  | Page 2, line 16, for "metal-stable" read "meta- |
|    | s   |  | stable"   |
|    | h.  |  | Page 2, line 45, for "base" read "haze"         |
| 20 | tr  |  | Page 3, line 59, for "hydrogen" read "hydro-    |
|    | ha  |  | gels"   |
|    | ti  |  | THE PATENT OFFICE                               |
|    | in  |  | 1st February 1971                               |
|    | tu  |  |   |
| 25 | tir |  |   |
|    | all |  |   |

to remove both the haze developed during production or on standing prior to final processing and also haze forming materials which will develop haze during the time the beer is standing after the final processing but before being consumed. It is desirable that the materials used for treating the beer do not remove from the beer components which are essential to the character of the beer such as flavour forming components, head-forming components and colourings.

Various materials such as bentonites, active carbon, nylon, polyvinyl pyrrolidone and certain silicas have previously been proposed for this purpose and are to a greater or lesser extent effective. However, the cost of such treatment arising both from the materials used and from processing costs such as filtration and storage are not insignificant and any

120 Å and separating the silica from the beer.

The definition of a silica hydrogel as given in the literature is not always clear and silica xerogels and silica hydrogels have many similar features. However, in this specification and claims these two types of silica gel are clearly distinguished as follows. A silica xerogel is considered to be a three-dimensional network of ultimate particles of polysilicic acid the size and packing of which determine the surface area and pore volume. Furthermore polymerisation of the polysilicic acid can be induced with the aid of an aqueous phase but this results only in the solution of the polysilicic acid and subsequent redposition to produce larger particles. This is evidenced by the fact that the degree of packing or total pore volume remains unchanged whilst the surface area is diminished. In the hydrogel state the

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SEE ERRATA SLIP ATTACHED

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polysilicic acid polymer exists as a semi-rigid mass. There exists a continuous water phase which promotes further growth by polymerisation and changes in packing density. The extent of the growth and change depends upon time, pH and temperature hence the hydrogel is a dynamic system and remains as such until the shrinkage forces introduced by the partial removal of the aqueous phase lead to the irreversible production of a xerogel "pore" system. It will therefore be appreciated that xerogel and hydrogel can readily be distinguished by the fact that pore volume as well as surface area change on the hydrothermal treatment of hydrogel hence the hydrogel is in a metal-stable state and the xerogel is in a stable form.

Hitherto in considering hydrogels in connection with surface area and pore volume, these characteristics have been defined in terms of the xerogel derived from the hydrogel in question, but methods used previously on xerogels have now been applied to hydrogels so that the surface area, pore volume and mean pore diameter can be deduced directly from a hydrogel. The pore volume (P.V.) of a silica hydrogel within limits is related to the water content of the gel. A sample of the hydrogel is weighed into a container which is then connected to a vacuum pump. When the pressure has dropped considerably (to about 0.1 mm. mercury) and most of the water has been removed, heating is started and the surface area of the sample determined using a conventional adsorption technique. After this, the sample is reweighed to find the actual weight of silica employed and the appropriate pore volume is calculated from:

$$P.V. = \frac{\% \text{ water}}{100 - \% \text{ water}} \text{ cc/g}$$

40 The mean pore diameter (MPD) is calculated from:

$$M.P.D. = \frac{4 W \times 10^4}{S(100-W)} \text{ \AA}$$

where  $W$  is weight % water in hydrogel and  $S$  is surface area of hydrogel,  $\text{m}^2/\text{gSiO}_2$ .  
 45 One accepted indication of the base reducing or stabilising efficiency of silicas used in the treatment of beers is the "saturated ammonium sulphate precipitation limit" test. In this test saturated ammonium sulphate solution is added to samples of treated and untreated beer and the quantity of solution required to cause a sudden increase in turbidity as measured by a reflectometer, is measured. The difference in quantity required by the treated and untreated beer, often expressed as  $\Delta m_1 \text{ SASPL}$ , is an indication of the haze reducing efficiency of the silica under test.

The head retention values (HRV) referred to in the present specification were determined by the following test.

Samples of beer were treated at  $0^\circ\text{C}$  with a sample of silica (1 g. as  $\text{SiO}_2$  per litre) and left standing for 5 minutes or 24 hours. Then the silica was filtered off. The treated beer was carefully run into a tube to a height of 10 cm., the tube having at its lower end a sintered glass disc through which carbon dioxide gas can be bubbled into the beer to form a head of foam. Bubbling is continued to a pre-determined height (32.5 cm.) and then the gas supply is reduced to just support the beer on the disc whereupon the foam starts to collapse. The head retention value is 1.44 multiplied by the time in seconds taken for the boundary between the level of the liquid beer and the bottom surface of the foam to pass between marks at 5 and 7.5 cm. on the tube.

Whilst we do not wish in any way to be bound by the following theories these theories do offer a possible explanation of the way in which the process of the present invention works.

It appears to be possible that the stability of foam on beer ("head") is dependent on a positive or boosting and negative or suppressing head factor and that these two factors are constituted by materials of significantly different particle size or shape hence by selecting silica hydrogel having a closely defined MPD the negative factor can perhaps be preferentially or selectively removed.

Accordingly in a preferred embodiment of this invention the mean pore diameter of the silica hydrogel is from 40 to 80  $\text{\AA}$ .

It will be understood that the MPD is an average figure and can be the result of a wide or narrow actual distribution of pore widths and the preferred silicas for use in this invention have a wide distribution of pore widths and not a relatively narrow one as has been the case with hitherto proposed high pore volume xerogels and with certain precipitated silicas to which have been ascribed "mean pore diameters".

For efficient operation of the process of this invention and particularly to produce the best results in respect of contact time of beer and silica and ease of separation of beer from the silica it is desirable that a significant proportion of the silica is present as fine particles. The average particle size of the silica is preferably less than 20 microns.

As with the MPD discussed above, the actual particles on which the average figure is based can be made up in various ways and for the process of this invention it is desirable that at least 10% by weight of the silica is made up of particles smaller than 10 microns. Whilst it will be appreciated that the accurate assessment of particle size is

difficult when the particles are less than about 3 microns the following Table I indicates that for good  $\Delta$  ml SASPL figures a significant number of particles less than 5 microns is desirable.

	TABLE I	
	$\% i < 5\mu$	$\Delta$ ml SASPL ( $\Delta$ ml)
	38.4	2.2
	9.9	2.0
10	7.7	1.7
	0.4	1.6
	0.1	1.2

Accordingly silica hydrogels having at least 10% by weight of their particles less than 5 microns are particularly useful.

The quantity of silica used in the treatment of beer will be to an extent dependent on the actual hydrogel selected and on the quality and age of the beer to be treated.

In general using the above defined silica hydrogel it will not normally be necessary to use more than 1 g. of silica per litre of beer to be treated.

In a further preferred form of the invention the pH of a hydrogel dispersion, containing at least 5% by weight of silica, is in the region of the isoelectric point of the silica that is to say having a pH about 2. Hydrogels having a pH between 2 and 1.5 show outstandingly good characteristics when judged by the  $\Delta$  ml SASPL and their stability.

The hydrogel for use in this invention may be used in the form of a slurry although the powder form is preferred.

The hydrogels useful in the present invention may be prepared by known techniques. A common method of preparation involves the addition of sulphuric acid 1.33 specific gravity (SG) to sodium silicate (3.3:1)  $\text{SiO}_2 : \text{Na}_2\text{O}$  and 1.315 SG) and can conveniently be carried out in a jet mixer. The sol produced is allowed to form a gel structure at a pH of 0.22 and synerise in a suitable container for a period of up to 6 hours. The gel is then broken into small pieces and washed with water at a pH of about 4 to remove a substantial proportion of the electrolyte, the

washing period can be up to 15 hours. The pieces of gel are then washed and milled to produce hydrogel 32 for use in this invention.

A sample of this hydrogel 32 was air-dried to provide hydrogel 40 and a sample of this material further air-dried to provide hydrogel 48. A sample of hydrogel 48 was then oven-dried to provide xerogel A and as is well-known, such a drying step causes the pores to close to a significant extent.

Table II shows the various characteristics of hydrogen 32, 40 and 48 and of xerogel A. In addition xerogels B and C have been tested for comparative purposes.

The tests of stabilising efficiency  $\Delta$  ml SASPL and head retention value were those described earlier and were applied to a normal pale ale as normally sold as a bottled beer.

The surface areas shown in Table II were determined by the "one point method". This is a simplified method of determining the surface area of a particulate solid by use of the BET equation (Brunauer, Emmett & Teller). This refers to the nitrogen absorption method given in J. Amer. Chem. Soc. 59 (1937) pp. 1553—1564 (Emmett & Brunauer) and 60 (1932) pp 309—310 (Brunauer, Emmett & Teller). Generally with the BET method surface areas are determined by carrying out a series of experiments to produce data from which a nitrogen adsorption isotherm is plotted on a graph and this particular method of determination gives a straight line. By determining the quantity of gas absorbed at one fixed point and assuming a given value of intercept it is possible to determine the surface area from a single determination. When materials of the same general character are being investigated this approximation is satisfactory because the position of this intercept has been established from previous experience. In the case of silica therefore, all that is necessary is to carry out adsorption determination at a relative pressure of about .2 and determine the volume of nitrogen adsorbed at the boiling point, i.e. 77°K, this is the so-called "one point method" of determining the surface area.

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TABLE II

	Silica 1 g./litre	Surface area (N <sub>2</sub> ) m <sup>2</sup> .g <sup>-1</sup>	Water Content %	Mean Pore Dia. Å	Particle Size		Stabilising efficiency		Head retention values (secs)		
					% >40 $\mu$	% 10 > $\mu$	APS $\mu$	SASPL ml (5 mins)	Δ ml SASPL	HRV 5 mins	Δ secs
Control	—	—	—	—	—	—	—	1.2	—	141.1	—
Xerogel A	984	8	24	0	16.5	15.0	1.8	0.6	152.9	+11.8	
Hydrogel 48	1011	52	43	0	16.0	15.0	2.9	1.7	144.4	+ 3.3	
Hydrogel 40	1033	60	58	1.1	15.9	15.3	3.2	2.0	145.3	+ 4.2	
Hydrogel 32	1006	68	84	4.7	14.6	16.4	3.2	2.0	144.3	+ 3.2	
Xerogel B	360	0	103	3.5	11.6	23.4	3.1	1.9	144.6	+ 3.5	
Xerogel C	360	0	103	0	32	12	3.4	2.2	131	-10.1	
Hydrogel 32 10 g./litre	1006	68	84	4.7	14.6	16.4			123.0	-18.1	
Xerogel B 10 g./litre	360	0	103	3.5	11.6	23.4			92.2	-48.9	

**WHAT WE CLAIM IS:—**

1. A process for the treatment of beer which comprises contacting the beer with a silica hydrogel having a surface area of at least 700 m<sup>2</sup>/g. and a mean pore diameter from 30 to 120 Å and separating the silica from the beer.

2. A process as claimed in Claim 1, in which the mean pore diameter of the silica is from 40 to 80 Å.

3. A process as claimed in Claim 1 or Claim 2, in which the average particle size of the silica is less than 20 microns.

**4. A process as claimed in Claim 3, in which at least 10% by weight of the hydrogel is made up of particles smaller than 10 microns.**

5. A process as claimed in Claim 4, in which at least 10% by weight of the hydrogel is made up of particles smaller than 5 microns.

6. A process as claimed in any one of the preceding claims, in which the distribution of pore sizes on which the mean pore diameter is based is a wide one.

7. A process for the treatment of beer, which comprises mixing with the beer a silica

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which at least 10% by weight of the hydrogel is made up of particles smaller than 10 microns.

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which at least 10% by weight of the hydrogel is made up of particles smaller than 5 microns.

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which at least 10% by weight of the hydrogel is made up of particles smaller than 10 microns.

which comprises mixing with the beer a silica

hydrogel as defined in Table II and separating the silica from the beer.

5 8. A process as claimed in any one of the preceding claims in which the hydrogel contains at least 5% by weight of silica and the pH is between 2 and 1.5.

9. Beer treated by a process as claimed in any one of the preceding claims.

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Chartered Patent Agent.

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